Lifetimes of *d* holes in Cu and Au: Full-potential LMTO approach

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(Received 17 October 2002; published 1 July 2003)

We report on theoretical studies of hole lifetimes in Cu and Au by means of the *ab initio* all electron full potential linear method of ''muffin-tin'' orbitals approach. We find that the momentum-averaged *d*-hole lifetimes in Cu, Au deviate much less from the lifetimes of holes in free-electron-like *s*,*p* bands than it was found in previous *ab initio* studies. However, at symmetry points *L* and *X* and along the *X*-*W* direction of the Brillouin zone the differences between the lifetimes of *d* holes and *s*,*p* holes are big. The lifetime of a hole in the top X_5 *d* state of Cu is in good agreement with the experimental data. The lifetimes for lower *d* states deviate from experimental results, which we refer to neglecting spin-orbit coupling and interactions described by higher order terms of many-body perturbation theory. We discuss the calculational details responsible for the precision of the lifetime evaluations.

DOI: 10.1103/PhysRevB.68.045102 PACS number(s): 71.15.−m, 78.47.+p, 79.60.−i

I. INTRODUCTION

A great progress in the study of the dynamics of photoexcited hot electrons have been achieved recently by using two-photon time-resolved photoemission spectroscopy for measuring the electron relaxation times in bulk metals,[1–6] at clean metal surfaces[7–11] and at metal surfaces covered with single atoms and molecules.[11–15] A number of important results have been obtained for the hole dynamics in metals due to the use of high-resolution angle-resolved photoemission spectroscopy.[16–20] The application of scanning-tunneling microscopy was also successful.[21] For the bulk metals the electron and hole excitations in Cu, Ag, and Au were most extensively studied.[1–4,16] In particular, Gerlach *et al.*[18,19] have performed detailed investigations of the hole excitations in *d* states of Cu (Ref. 18) and Ag (Ref. 19), including accurate estimation of phonon and defect scattering contributions to the measured hole linewidth.

Recent theoretical investigations of the electron and hole excitations in metals have mostly been performed by using *GW* approximations for the quasiparticle self-energy.[22,23] A different approach based on the Boltzmann equation has been used by Knorren *et al.*[5,24] to study the excitations in transition metals. The *GW* approach was employed to study the lifetimes of electron excitations in simple metals Mg, Be,[25] and Al,[25–27] in noble metals,[25,26,28–30] as well as in transition metals Nb, Mo, Rh, Pd,[27,31,33] Y, and Ru.[33] Hole lifetimes have been studied for Al,[27] for noble[18,30–32,34] and transition[27,31] metals. All the cited *GW* calculations were based on the local-density approximation of the density-functional theory (LDA) for computing electronic band structure. In Refs. 25,26,28,29,32–34 the pseudopotential method with plane-wave basis set (PPW) has been used, whereas in Refs. 27,30,31 the linear method of ''muffin-tin'' orbitals in the atomic sphere approximations (LMTO ASA) has been employed.

In many cases the *GW* approach correctly reproduces the changes of experimental electron relaxation times with the excitation energy. In particular, reasonable overall agreement between time-resolved two-photon photoemission data and *GW* calculations is obtained for electron excitations in noble metals (for a review, see Ref. 30). However, big discrepancies between theoretical and experimental results take place for *d* holes in Cu and Ag. Namely, the lifetimes of holes in the top *d* bands as calculated both by the PPW *GW* and LMTO ASA *GW* approaches appear to be almost twice longer than the experimentally derived lifetimes.[18,19,30,32] The origin of this disagreement is not still clear.

Recently two new versions of the *GW* method have become available: full-potential linear method of muffin-tin orbitals (FP LMTO *GW*) (Ref. 35) and full-potential linear augmented plane-wave method.[36] An advantage of these new methods with respect to the previous PPW *GW* and LMTO ASA *GW* methods is the invocation of mixed basis sets that include both atomiclike muffin-tin orbitals and plane waves. One should therefore expect that these methods are better adapted for the calculations of both free-electron-like states and localized *d* states, e.g. all the relevant states in noble metals. Taking into account the nonspherical components of the crystalline potential, these methods potentially can provide more correct calculations of the transition probabilities, and consequently the quasiparticle lifetimes. The FP LMTO *GW* methods contain all the steps of the *GW* calculations: evaluation of LDA band structure, calculations of dielectric function and screened potential, solution of quasiparticle energy equation, and calculations of self-energy corrections to LDA eigenvalues. So comparing the FP LMTO *GW* results with the previous *GW* calculations and with the experimental results, we can evaluate the lifetimes of quasiparticles in band states and also get insight into the physics involved in the *GW* calculations.

In this paper we present the results of the FP LMTO *GW* calculations for the lifetimes of hole excitations in Cu and Au. We analyze the discrepancies between the experimental data and the calculated lifetimes and discuss the physical effects that underlie these discrepancies. The calculations shed light on the drawbacks of the earlier *GW* lifetimes computations and help to evaluate some proposals aimed to improve the lifetimes calculations.

II. METHOD OF CALCULATION

The FP LMTO *GW* method is a descendant of the LMTO ASA method that was well documented in Refs. 22,37. Hence we outline only the main steps of the FP LMTO calculations and the most important differences between the LMTO ASA and FP LMTO approaches.

The Hedin's *GW* approximation[22] for the self-energy is

$$\Sigma(\mathbf{r},\mathbf{r}',\omega)=\frac{i}{2\pi}\int d\omega' G(\mathbf{r},\mathbf{r}',\omega+\omega')W(\mathbf{r},\mathbf{r}',\omega'), \quad (1)$$

where W is the screened Coulomb potential and G is the Green's function. As the majority of the *GW* method versions, the FP LMTO *GW* method invokes the noninteracting Green's function, and the random-phase approximation (RPA) for W. So G and W are calculated from the LDA eigenvalues and eigenvectors obtained within the FP LMTO method. The expectation value of the operator $\Delta\Sigma(\omega)=\Sigma(\omega)-V_{LDA}^{xc}$, where V_{LDA}^{xc} is the LDA exchange-correlation potential, determines the many-body self-energy corrections to the LDA eigenvalues $\epsilon_{\mathbf{q},i}$ through the Dyson's equation (i is the band index and $\mathbf{q}$ is the wave vector)

$$E_{\mathbf{q},i}(\omega)=\epsilon_{\mathbf{q},i}+\langle\psi_{\mathbf{q},i}|\Delta\Sigma_{\mathbf{q},i}(\omega)|\psi_{\mathbf{q},i}\rangle. \quad (2)$$

The roots of this equation in complex ω plane can be found by direct search. Usually the Dyson's equation is simplified by retaining only the linear part of the dependence of $\Delta\Sigma$ on the real part of ω. In this approximation the self-energy correction to $\epsilon_{\mathbf{q},i}$ is

$$\Delta\epsilon_{\mathbf{q},i}=E_{\mathbf{q},i}-\epsilon_{\mathbf{q},i}=Z_{\mathbf{q},i}\Delta\Sigma_{\mathbf{q},i}(\epsilon_{\mathbf{q},i}), \quad (3)$$

where

$$Z_{\mathbf{q},i}=\left[1-\frac{\partial \mathrm{Re}\Delta\Sigma_{\mathbf{q},i}(\omega)}{\partial\omega}\right]^{-1}_{\omega=\epsilon_{\mathbf{q},i}} \quad (4)$$

is the renormalization factor. Very often the so-called ''on energy shell'' approximation $Z=1$ is used for calculations of electron and hole lifetimes.[19,25,26,28,29,32,33] Here we present the lifetime evaluations both with ''calculated Z'' and within the ''on shell'' approximation. Recently in Ref. 34 the lifetimes of holes in copper have been calculated also, based on the PPW approach, by direct search in complex ω plane. The imaginary part of the self-energy correction gives the linewidth of the quasiparticle excitation, and the inverse value determines the lifetime of a quasiparticle,[23]

$$\tau_{\mathbf{q},i}^{-1}=2|\mathrm{Im}\Delta\epsilon_{\mathbf{q},i}|. \quad (5)$$

In the FP LMTO method the crystal space is separated into nontouching atomic spheres and interstitial region. Contrary to the LMTO ASA method, all the nonspherical components of the crystal potential in the interstitial region are taken into account. Inside the atomic spheres the self-consistent LDA eigenfunctions are expanded into a set of muffin-tin orbitals and their energy derivatives. Inside the interstitial space the LDA eigenfunctions are expanded into a set of plane waves[38]. In order to expand the products of the LDA eigenfunctions, when calculating polarization function, a mixed basis set is employed. It includes the intersphere basis functions constructed from products of muffin-tin orbitals, and a set of plane waves. The intersphere basis functions of such expansions are created by the prescriptions of the LMTO ASA *GW* method.[22,37,38] So we calculate the polarization matrix of a crystal within the random-phase approximation,

$$P_{i,j}(\mathbf{q},\omega)=\sum_{\sigma,t,\mathbf{k}}\sum_{n}^{occ}\sum_{n'}^{unocc}\frac{1}{t\omega-\epsilon_{\mathbf{k}+\mathbf{q},n'}+\epsilon_{\mathbf{k},n}+i\delta}\times\langle B_{\mathbf{q},i}\psi_{\mathbf{k},n}|\psi_{\mathbf{k}+\mathbf{q},n'}\rangle\langle\psi_{\mathbf{k}+\mathbf{q},n'}|\psi_{\mathbf{k},n}B_{\mathbf{q},j}\rangle. \quad (6)$$

Here $B_{\mathbf{q},i}$ are the functions of the mixed basis set. The summation includes terms with $t=\pm1$ (electrons and holes) and spin coordinate σ. The following calculations include the evaluation of the matrix of the density-density correlation function $\mathbf{R}$, the matrices of dielectric and inverse dielectric functions, $\boldsymbol{\epsilon}$ and $\boldsymbol{\epsilon}^{-1}$, and the matrices of bare Coulomb interaction $\mathbf{v}$ and of dynamically screened Coulomb interaction $\mathbf{W}$, all with the functions of the mixed basis set,

$$\mathbf{R}=\mathbf{P}+\mathbf{PvR}, \quad (7)$$

$$\boldsymbol{\epsilon}=1-\mathbf{vP}, \quad (8)$$

$$\boldsymbol{\epsilon}^{-1}=1+\mathbf{vR}, \quad (9)$$

$$\mathbf{W}=\boldsymbol{\epsilon}^{-1}\mathbf{v}. \quad (10)$$

Having evaluated $\mathbf{W}$, we calculate the imaginary part of the self-energy operator by the receipts of the LMTO ASA *GW* method.[22,37,38] The real part of the operator is calculated by the Hilbert transform. Then the momentum-resolved lifetimes of excitations are calculated at the individual wave vectors by Eq. (5) and averaged over momentum vectors. The number of wave vectors was equal in our calculations to 256 in the irreducible part of the Brilloin zone (BZ) (8000 in the whole BZ). The used value of the broadening parameter δ of Eq. (6) was varied between 0.001 and 0.005 Hartree units (0.027 and 0.136 eV). When constructing the basis functions of the polarization matrix, all the products $s\times s$, $s\times p$, $s\times d$, $p\times p$, $p\times d$ have been employed. When calculating the polarization matrix by Eq. (6), only the valence band states have been taken into summation. Testing calculations performed with smaller numbers of momentum vectors have shown that with the inclusions of core states the lifetime values at the excitation energies below 5 eV practically do not change, because of too low LDA energy of the highest core states (-71 eV for $3p$ Cu states and -59 eV for 5p Au states).

III. RESULTS AND DISCUSSIONS

The FP LMTO results for electron excitations in Cu, Au are very close to those obtained from LMTO ASA calculations.[30] A number of significant differences arises in the evaluations of hole lifetimes. In Fig. 1 we compare momentum-averaged and symmetry-point hole lifetimes in

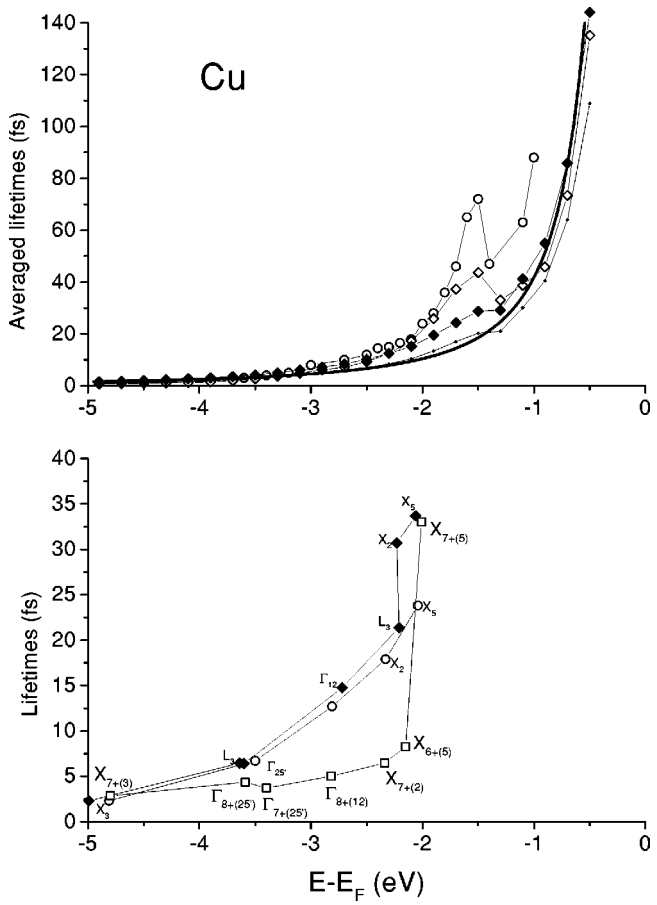

FIG. 1. The theoretical and experimental data on lifetimes of hole excitations in copper. *Upper panel*: The theoretical momentum-averaged lifetimes of hole excitation with respect to the binding energy. Open circles are the results of PPW *GW* calculations within ''on energy shell'' approximation (Ref. 32). Open diamonds are the data of LMTO ASA calculations (Ref. 31). Big solid diamonds represent the results of the FP LMTO *GW* calculations with calculated *Z*, whereas small solid diamonds are the FP LMTO *GW* results with $Z=1$ (on energy shell approximation). Thick solid line represents the hole lifetimes as calculated within the Fermi-liquid theory at the value of electron-density parameter $r_s=2.1$. *Lower panel*: The calculated and experimental *d*-hole lifetimes in some symmetry points of the Brilloiun zone. Open squares are the experimental data of Ref. 18. Solid diamonds are the results of our FP LMTO *GW* calculations, and open circles are the data of the PPW *GW* calculations of Ref. 34. In order to provide comparisons with the experimental data, the FP LMTO results have been shifted by -0.4 eV.

Cu with available experimental data[6,18] and with the PPW *GW* calculation results.[32,34] The holes at energies above -1.5 eV belong to the free-electron-like 4p-states. Similar to the LMTO ASA calculations, the lifetimes of these holes demonstrate small dispersion with respect to the direction of the wave vector, and they are well approximated by the RPA version of the Fermi-liquid theory[39] with an adjusted value of electron-density parameter $r_s=2.1$.[30] The peak in the averaged lifetime curves at lower energy belongs to the holes in $3d$ states. The origin of the discrepancies between the lifetimes of free-electron-like holes and *d* holes was discussed in Refs. 6,18,30. Due to different symmetry of the states, the $3d$-$4p$ transition probabilities are smaller than the $4p$-$4p$ probabilities, which results in longer lifetimes of holes in the top *d* states. Because of the large density of *d* states, the number of states available for the damping of *d* holes increases rapidly with the increase of the *d* state binding energy, thus causing a shortening of lifetimes. Qualitatively, this effect is well reproduced by the *GW* approach. However, in the PPW *GW* calculations[32] the maximum (peak) value of the averaged *d*-hole lifetimes was bigger by a factor of 2 than the available experimental data. The calculations with the muffin-tin orbital basis set[30] led to a markedly lower peak in the *d*-hole lifetimes, whereas in the new FP LMTO calculations this peak disappears leaving only a weak shoulder.

Hence the results of the FP LMTO calculations show that the increase of the averaged hole lifetimes at the upper edge of the *d* band was overestimated in previous theoretical calculations. In order to check the precision of theoretical calculations, we compare, in the lower panel of Fig. 1, the theoretical results for some symmetry points of the Brillouin zone with the available experimental lifetimes, as obtained by angle-resolved photoemission[18] and time-resolved two-photon photoemission[6] spectroscopies. Besides the FP LMTO data, the results of recent PPW *GW* calculation,[34] are also given in this panel. The numerical data on lifetimes, together with the results of the previous LMTO ASA calculation[30] and PPW calculations[34] are compared with experimental data in Table I. Gerlach *et al.*[18] decomposed the measured linewidth Γ_{exp} (inverse lifetime) into three terms: $\Gamma_{exp}=\Gamma_{hh}+\Gamma_{h\text{-}ph}+\Gamma_{hd}$, where Γ_{hh} is the contribution from hole-hole interactions, $\Gamma_{h\text{-}ph}$ is the contribution from hole-phonon scattering, and Γ_{hd} is the contribution from hole-defect scattering. The experimental data of Ref. 18 shown in Fig. 1 and in Table I represent only the Γ_{hh} values. The lifetime value of Ref. 6, 24 ± 3 fs, for the highest $X_{5(7+)}$ *d* state is smaller than the photoemission result of Ref. 18, 33 ± 7 fs. However, the value of Ref. 6 contains the hole-defect scattering contribution Γ_{hd}. Having corrected 24 fs with the value $\Gamma_{hd}=8$ meV of Ref. 18, we obtain $\tau=32$ fs. Hence the experimental data on the lifetime of the $X_{5(7+)}$ state are in good mutual agreement, and also in excellent agreement with our FP LMTO lifetime $\tau=33.7$ fs. The previous LMTO ASA calculations, in which only muffin-tin basis function were used, gave for the X_5 state the lifetime value 40% higher than the experimental one, whereas PPW *GW* data invoking only plane-wave basis states produced a value 30% lower.

For binding energies higher than that of the X_5 state the FP LMTO symmetry-point lifetimes are close to the PPW *GW* results. Slightly worse, though also good, is the agreement with the LMTO ASA data. However, the experimental lifetimes demonstrate a sharp decrease near the top *d*-band energy, and all the calculated lifetimes appear to be longer than the experimental ones.

In Fig. 2 we show the analogous data for gold. Notice that the averaged lifetimes as calculated within the PPW method, Ref. 32, show a more complicated energy change whose origin is not clear. As in the case of Cu, the LMTO ASA, and especially FP LMTO calculations produce much less values of averaged lifetimes. The symmetry-point lifetime values,

TABLE I. The quasiparticle lifetimes (in fs) in some symmetry band states of copper according to the LMTO method, PPW method, and corresponding experimental data

		LMTO ASA (Ref. 30)	FP LMTO	On-shell FP LMTO	PPW (Ref. 34)	On-shell PPW (Ref. 34)	Experimental data
	X_5	47.1	33.7	23.6	23.8	79.4	32 ± 3 (X_{7+}, Ref. 6)[a]
							33 ± 7 (X_{7+}, Ref. 18)
Lifetimes	X_2	47.5	30.7	21.2	17.9	88.0	6.5 (X_{7+}, of Ref. 18)
of d states	L_3	23.5	21.4	15.0			
	Γ_{12}	12.6	14.8	9.9	12.7	25.0	5.0 (Γ_{8+}, Ref. 18)
	$\Gamma_{25'}$	3.2	6.4	4.2	6.7	6.8	4.4 (Γ_{8+}, Ref. 18),
							3.7(Γ_{7+}, Ref. 18)
	L_3	3.2	6.4	4.2			
	X_3	0.6	2.3	1.5	2.3	1.1	2.8(X_{7+}, Ref. 18)

[a]Corrected with the hole-defect interaction—see text.

given in the lower panel, also smoothly decrease with binding energy; we are not aware of corresponding experimental data.

As follows from Figs. 1 and 2, the smooth change of the averaged lifetime is relatively well reproduced by the Fermi-liquid theory with effective r_s parameter obtained by fitting to the first-principles results[30] both for Cu and Au. However, this smooth behavior conceals very strong momentum dependence of the d-hole lifetimes. To illustrate this, we show in Figs. 3 and 4 the lifetimes of d holes in Cu and Au for the L-Γ, Γ-X, and X-W directions. The changes of lifetimes along these directions correspond well to the phase space rule: the lower is the energy of a d state, the more the states available for the damping of holes, and the shorter is the lifetime of the state. So qualitatively the lifetime dispersion curves resemble usual energy bands. The dispersion curves shown in Figs. 3 and 4 are similar to those calculated within LMTO ASA.[30] The greatest differences are found for the X_5 and X_2 states. In comparison with LMTO ASA data, the lifetimes of these states in Cu(Au) are shorter by 35(15)% and 60(20)%, respectively. The LMTO ASA lifetimes of all L, all Γ, W_1, and W_3 states do not differ much from the FP LMTO lifetimes.

When discussing the differences between the calculated and experimental lifetimes one can think *a priori* of the following origins for such discrepancies: the absence of spin-orbit coupling in the LMTO and PPW band structure calculations invoked to construct the Green's function, the approximate way of solving the nonlinear equation for the quasiparticle energy (the use of ''calculated Z'' or ''on energy shell'' approximations instead of complete direct search of the solutions), the neglecting of higher order terms of many-body perturbation theory, and the incompleteness of

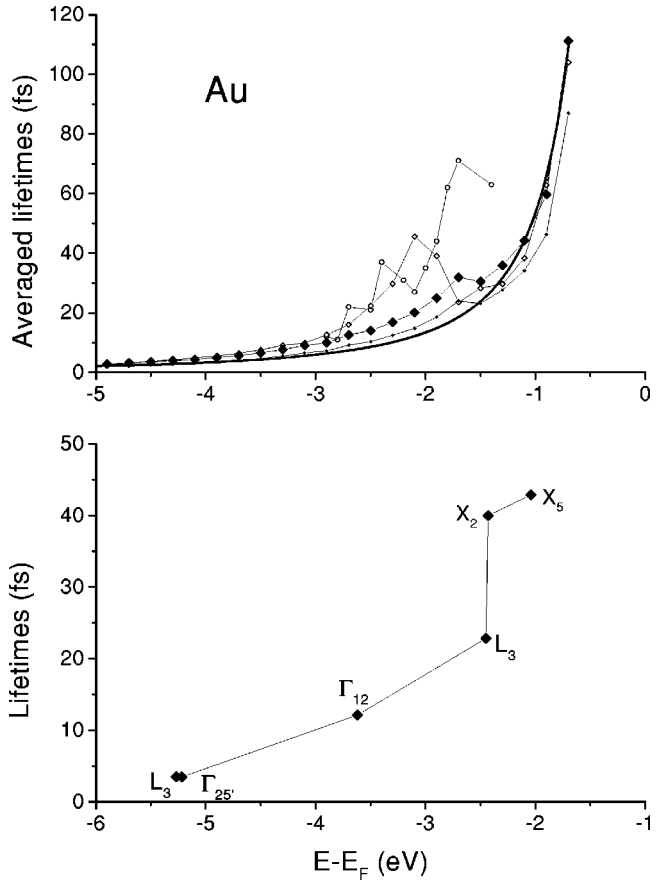

FIG. 2. Theoretical data on the lifetime of holes in gold. The notations are the same as in Fig. 1. Thick solid line represents hole lifetimes as calculated within the Fermi-liquid theory at the value of electron-density parameter $r_s=1.9$. The FP LMTO results shown in the lower panel have been shifted by -0.5 eV in order to align with the experimental binding energies.

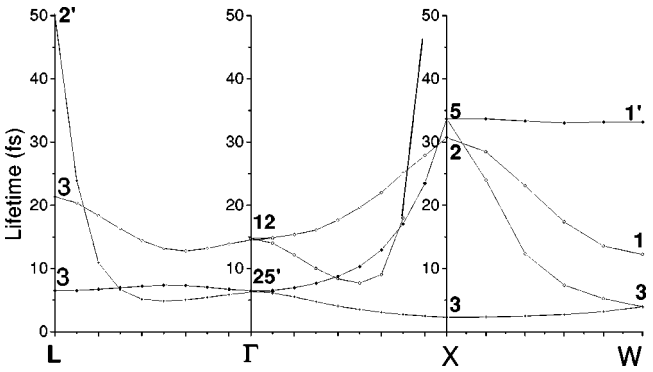

FIG. 3. The d hole lifetimes in Cu for the states along the L-Γ, Γ-X, and X-W directions.

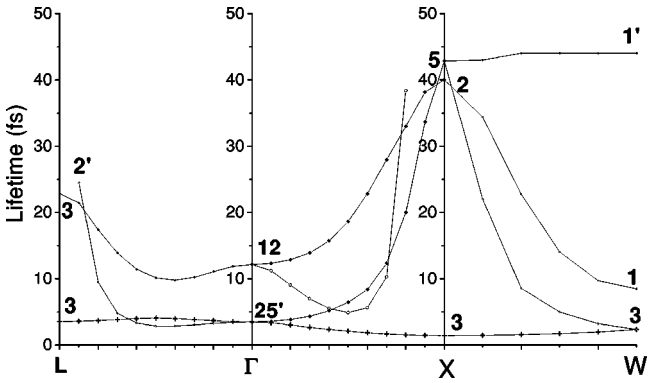

FIG. 4. The *d* hole lifetimes in Au for the states along the L-Γ, Γ-X, and X-W directions.

the basis sets used to expand LDA eigenfunctions as well the response function.

The importance of including the spin-orbital coupling into the band structure calculations is well evident. It follows from the big difference in the experimentally derived lifetimes of the states X_{7^+} and X_{6^+} which are the counterparts of the nonrelativistic state X_5 split by the spin-orbit coupling.

In Table II we compare some FP LMTO data on the Cu band structure with the PPW band structure data of Ref. 40 and with experimental results of Ref. 41. The data indicated as PPW LDA represent the PPW LDA one-electron energies whereas the PPW GW results include GW self-energy corrections. Well known drawbacks of the LDA band structures of noble metals Cu, Ag, and Au are the energies of *d* bands, which are closer to Fermi-level than the experimental ones. LDA also leads to slightly broader dispersion of the bands compared with photoemission results. As follows from the table, the GW self-energy corrections bring the energy of the top *d*-bands in better agreement with experimental data. However, the PPW GW calculations overestimate the self-energy corrections for lower *d* bands, and the corrected PPW GW *d* bands appear to be too narrow, while the widths of *d*-bands calculated within the FP LMTO LDA method are closer to experimental data.

Our FP LMTO GW calculations do not include self-energy corrections to LDA band energies. The FP LMTO band-energies are close to those of LMTO ASA method; so we deduce that the decrease of the $3d$-hole lifetimes from LMTO ASA to FP LMTO is related mainly with the changes of matrix elements, and not with the changes of the top energy and widths of the *d* bands. The most essential difference between the LMTO ASA and FP LMTO GW approaches is the extension of the FP LMTO basis set by plane waves. The inclusion of both numerical muffin-tin orbitals and plane waves permits a better description of LDA wave functions within FP LMTO approach. Due to this, the values of d-p transition probabilities becomes greater, hence the *d*-hole lifetimes shorten.

The question of an appropriate way of solving the equation for the energy of a quasiparticle is clarified by comparing the lifetimes evaluated within the calculated Z and on energy shell ($Z=1$) approximations. The averaged FP LMTO lifetimes evaluated in such two ways are shown in the top panels of Figs. 1 and 2. For the symmetry-point states, they are given in Table I. Typical values of Z for the LDA *d* states of copper vary from 0.6 to 0.8, and the difference between the averaged lifetimes calculated in these ways does not exceed 30%. For the top LDA *d* state of copper, X_5, the renormalization factor value is $Z=0.7$. The lifetime of a hole in this state calculated within the on-shell approximation is 23.6 fs, which is well below the experimental value. At higher binding energies all the lifetimes evaluated within the on-shell and the calculated Z approaches are much higher then the experimental data. As it follows from the lower panel of Fig. 1, a 30% decrease of the lifetimes within the on energy shell approximation slightly improves the lifetimes, but appears to be too small to bring them in good correspondence with experimental data. In Table I we also show the results of Ref. 34 calculated within the on-shell approximation. They differ from the experimental data and our on-shell calculations by a factor of 2–4; the origin of such discrepancies is not clear. The correctness of our calculations is supported by a close agreement with PPW lifetime calculations by Keyling *et al.*[29] for electrons excitation in Cu, Ag, and Au. For the states below Γ_{12}, a good agreement is observed also between our FP LMTO lifetimes and the lifetimes calculated in Ref. 34.

So we do not find that the employment of noncorrected

TABLE II. Theoretical, as calculated by the FP LMTO and PPW methods, and experimental band energies (in eV) in copper

		FP LMTO	PPW LDA (Ref. 34)	PPW GW (Ref. 34)	Experimental data (Ref. 41)
	Γ_{12}	−2.36	−2.27	−2.81	−2.78
Energies of bands	X_5	−1.63	−1.40	−2.04	−2.01
	L_3	−1.78	−1.63	−2.24	−2.25
	$\Gamma_{12}-\Gamma_{25'}$	0.81	0.91	0.60	0.81
Widths of *d* bands	X_5-X_3	2.92	3.23	2.49	2.79
	X_5-X_1	3.37	3.70	2.90	3.17
	L_3-L_3	1.43	1.58	1.26	1.37
	$L_3-L_{1'}$	3.42	3.72	2.83	2.91
Energies of s,p bands	Γ_1	−9.35	−9.79	−9.24	−8.60
	$L_{2'}$	−0.92	−1.12	−0.57	−0.85
Energy of $L_{1'}$-$L_{2'}$ gap		4.78	5.40	4.76	4.95

LDA band structure or the mentioned approximations in solving quasiparticle equation are essential drawbacks of the lifetime calculations. One should look for different ways to improve the method. It is well known that the *GW* approach based on the RPA approximations well accounts for the long-range screening, whereas short-range interactions which are important in materials with *d* orbitals are not well described.[22] It is therefore probable that the improvement of the self-energy calculations for *d* materials can be achieved by inclusion of higher terms of the many-body perturbation theory. Such corrections are not necessary for the holes in the top X_5 state whose damping is realized through the transitions into the $4p$ states. Recently, a number of methods have been developed for calculations of such terms. In Ref.[42], e.g., an *ab initio T*-matrix approach has been developed based on the LMTO ASA band structure calculations. The method takes into account multiple hole-hole intrasite scattering, and permits us to calculate more correctly the spectral function of *d*-electron materials. However, neither *ab initio* nor model evaluations of higher term contributions to the lifetimes have still been performed.

IV. CONCLUSIONS

Analyzing the results of the FP LMTO *GW* lifetime calculations, we find it important to distinguish between the highest X_5 *d* state of Cu and all the lower *d* states. For the hole in X_5 state, the FP LMTO *GW* calculations produce the lifetime value in very good agreement with experimental data. This confirms that the commonly used scheme of *GW* calculations does not contain essential drawbacks for the lifetimes of states damped through the Auger transitions between the *d* states and free-electron-like states.

However, we find that the decrease of calculated *d*-hole lifetimes with the increase of binding energy is too slow in comparison with the trend in experimental data. The inclusion of spin-orbit coupling is necessary for the lifetimes of the states subject to such interactions. We argue that the improvement of the lifetime calculations for the holes in lower *d* states will probably require an invocation of higher terms of many-body perturbation theory, presumably based on the *ab initio T*-matrix approach.

ACKNOWLEDGMENTS

Professor Takao Kotani is greatly acknowledged for the help in calculations and useful discussions. The support by the University of the Basque Country, the Basque Hezkuntza Saila, the Spanish Ministerio de Education y Cultura, and the Max Planck Grant for international cooperation are gratefully acknowledged. The useful discussions with T. Pitarke, A. Rubio, R. Keyling, and A. Marini are also acknowledged.

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